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Cite as: AIP Conference Proceedings **2049**, 020034 (2018); <https://doi.org/10.1063/1.5082439>
Published Online: 14 December 2018

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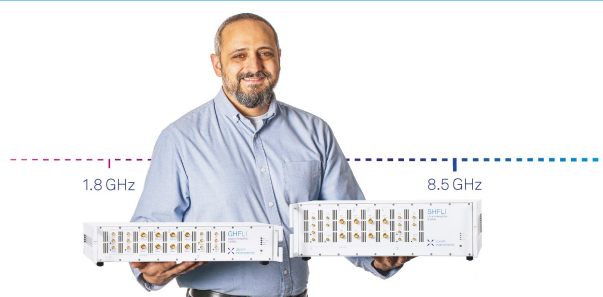
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Kinetic Parameters and Calorific Value of Biochar from Mahogany (*Swietenia macrophylla* King) Wood Pyrolysis with Heating Rate and Final Temperature Variations

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Abstract. Bio-Char was the solid product from pyrolysis and one of its important parameter was calorific value. Bio-char with high calorific value was yielded by a pyrolysis process with variation of heating rate and final temperature. The determination of kinetic parameter was also studied to get the proper conditions where the pyrolysis became easier to occur. The heating rate variations of pyrolysis were 10°C/min, 30°C/min and 60°C/min while the final temperatures were 350°C, 450°C, 500°C and 600°C. Mahogany wood was pyrolyzed with slow pyrolysis method in a batch reactor. It was found that activation energy became higher with the increase of heating rate and final temperature so the decomposition reaction will be more difficult. The calorific value of bio-char increased in the higher heating rate and also in the higher final temperature. The highest calorific value of biochar was 7512.96 cal/g and yielded in heating rate of 60°C/min with final temperature of 450°C. From all of the conditions performed, it was found that the calorific value of bio-char was higher than its raw material. Biochar, pyrolysis, Mahogany wood, calorific value

Keywords: biochar, pyrolysis, mahogany wood, calorific value.

INTRODUCTION

Mahogany is kind of wood that widely used in the industry involving furniture, construction, and decoration. A wood industry can produce the waste that consist 12-15% of sawdust, 25-35% of shavings and off-cuts, and 5-10% of trims and flawed woods, which is the total waste produced up to 50.8% of the raw materials (1). Mahogany is a biomass that contain a structural mixture (cellulose, hemicellulose, and lignin) where the each component will be decomposed in the different rates (2). One of the alternative method to manage the biomass waste is pyrolysis. The advantages of pyrolysis process are lesser CO₂ emission, higher quality of char and tar (3) and also higher conversion ratio (4).

Pyrolysis is a decomposition process of material in a high temperature without oxygen presence or with limited oxygen. The main product of pyrolysis are char, tar, and gas (5). There are some factor affect the pyrolysis process, such as temperature, heating rate, holding time, particle size, etc. (6). The important parameters of pyrolysis product are calorific value and activation energy.

The aim of this research is to study the effect of heating rate and final temperature of mahogany pyrolysis toward its kinetic parameters, like activation energy and also the calorific value of char yielded. Char with high calorific value can be used as renewable solid fuel that more efficient and environmentally friendly. The pyrolysis process was performed with slow pyrolysis method that can produce higher yield of char.

MATERIALS AND METHODS

a. Materials

The materials used in this research were mahogany wood waste which were collected from Bulusari, Ampel, Boyolali regency. Samples were crushed by crusher equipment until passing 20 mesh and then dried until the water content is not more than 10%. The calorific value of the sample was tested by ASTM D2015 standard method.

b. Methods

The pyrolysis process was conducted by taking 20 grams sample and put it in to sample holder. Sample holder was placed in the pyrolysis reactor then all the apparatus were arranged as shown at Fig.1. The heating rate variations of pyrolysis were 10 °C /min, 30 °C/min and 60 °C/min with same final temperature and holding time (450 °C and 5 min), while the variations of final temperatures were 350 °C, 450 °C, 500 °C and 600 °C and performed at the same heating rate and holding time (30 °C/min and 5 min). The heating temperature was increased every minute using thermocontroller. Char and tar yielded from pyrolysis process were tested for its calorific value using ASTM D2015 standard method.

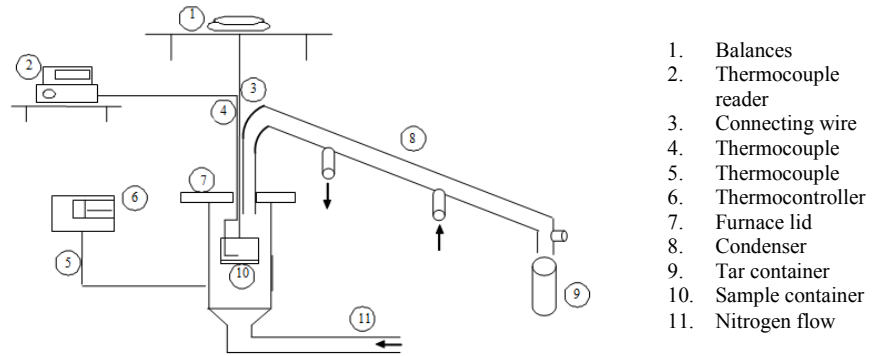


FIGURE 1. Experimental apparatus schematic

c. Activation energy determination

Activation energy of pyrolysis process can be calculated by Arrhenius equation using first order reaction as the following equation (7) :

$$\frac{dx}{dt} = Ae^{-\frac{E}{RT}}(1-x) \quad (1)$$

Where A is pre-exponential factor, E is activation energy, T is temperature, t is time, and x is pyrolysis conversion which can be calculated with this following equation.

$$x = \frac{w_0 - w}{w_0 - w_f} \quad (2)$$

Where w_0 is initial mass of the sample, w mass of the sample at the current temperature, and w_f is final mass of the char.

If β is heating rate constant, so:

$$\beta = \frac{dT}{dt} \quad (3)$$

By rearranging equation (1) gives

$$\frac{dx}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT \quad (4)$$

$$\frac{dx}{(1-x)} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT \quad (5)$$

By integrating equation (5) gives

$$-\ln(1-x) = \frac{A}{\beta} \int e^{-\frac{E}{RT}} dT \quad (6)$$

Since $\int e^{-\frac{E}{RT}} dT$ has no exact integral, $\int e^{-\frac{E}{RT}} dT$ can be expressed as an asymptotic series and integrated, with the higher order terms ignored, and equation (6) becomes

$$-\ln(1-x) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-\frac{E}{RT}} \quad (7)$$

$$-\frac{\ln(1-x)}{T^2} = \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-\frac{E}{RT}} \quad (8)$$

Expressing equation (8) into logarithmic form gives

$$\ln \left[-\frac{\ln(1-x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] \right] - \frac{E}{RT} \quad (9)$$

If $\frac{2RT}{E} \ll 1$ is assumed, so

$$\ln \left[-\frac{\ln(1-x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (10)$$

w and T for each minute can be used to determine x and by make a plot the relation between $\ln \left[-\frac{\ln(1-x)}{T^2} \right]$ and $1/T$, gives a straight line with $-E/R$ slope thus the activation energy can be defined.

RESULT AND DISCUSSION

a. Char yields

Fig. 2 shows the effect of heating rate and final temperature toward char yield in pyrolysis process. Higher final temperatures caused the decreasing of char yield which mean the weight-loss of the material was higher. This was because the primary decomposition of mahogany woods were higher in high temperatures(8). In addition, the decreasing of char yield also caused by secondary decomposition of char residue.

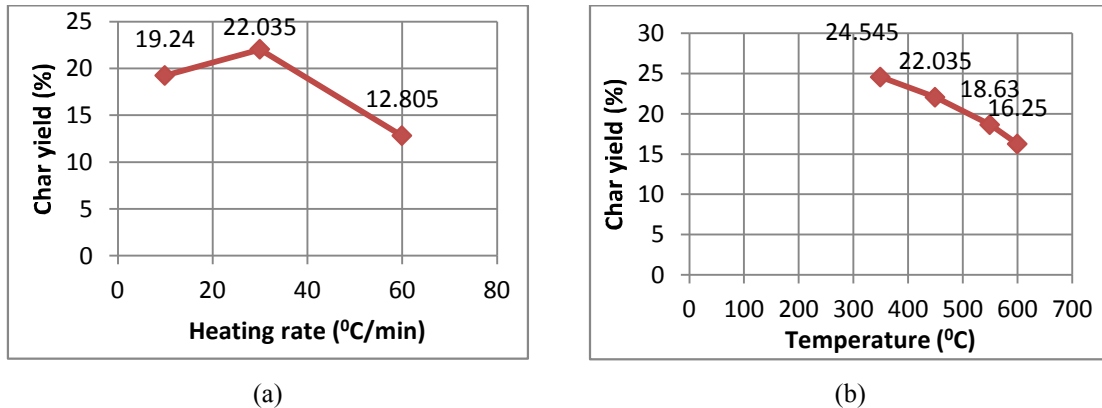
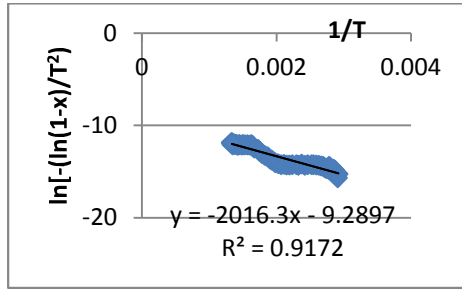


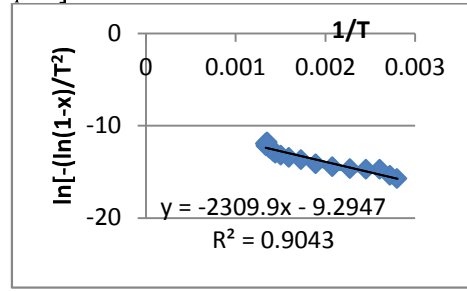
FIGURE 2. Effect of variations on char yield, (a) effect of heating rate and (b) effect of final temperature

b. Kinetic study

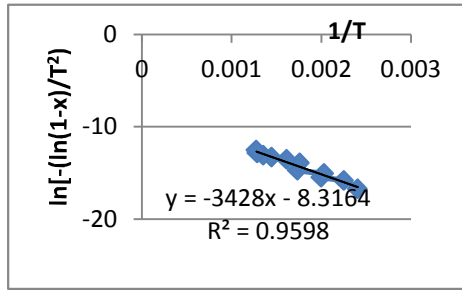
These following figures were the relation plot between $\ln \left[-\frac{\ln(1-x)}{T^2} \right]$ and $1/T$ in each variation.



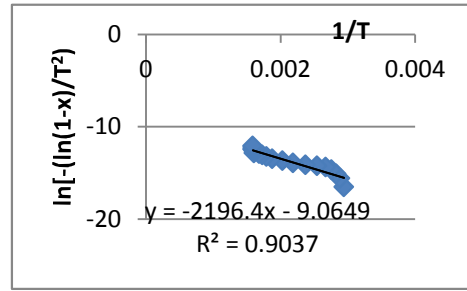
(a)



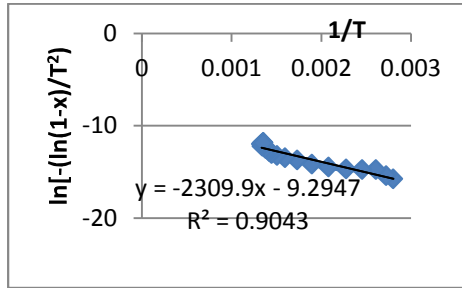
(b)



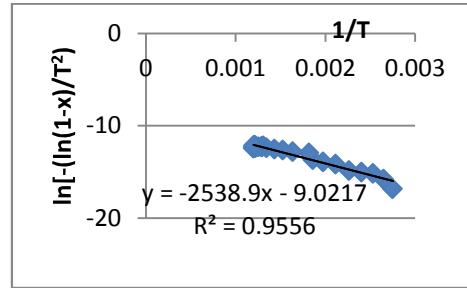
(c)



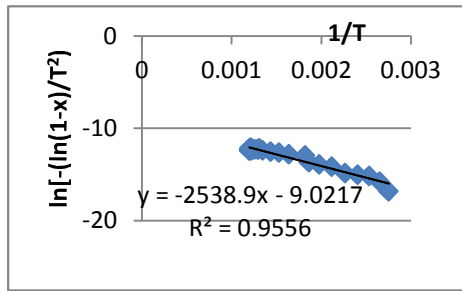
(d)



(e)



(f)



(g)

FIGURE 3. Plot $\ln \left[-\frac{\ln(1-x)}{T^2} \right]$ vs $1/T$ for each variations. (a) 10°C/min, (b) 30°C/min, (c) 60°C/min, (d) 350°C, (e) 450°C, (f) 550°C and (g) 600°C

Fig.3 shows R^2 value for all plots were ranged between 0.9 until 1. It shows there is an effect of temperatures toward decomposition reaction in pyrolysis. Activation energy for each variation was showed in Table 1 and 2.

TABLE 1. Activation energies on heating rate variation

Heating rate (°C/min)	Activation energy (kJ/mol)
10	16.76
30	19.20
60	28.50

TABLE 2. Activation energies on final temperature variation

Final temperature (°C)	Activation energy (kJ/mol)
350	18.26
450	19.20
550	21.10
600	21.34

Table 1 shows that the higher heating rate would increase the activation energy of pyrolysis. Activation energy was the amount of energy required for material to start being pyrolyzed. In higher heating rate, there were more alkyl free radicals produced. These reactive radicals will lead to stronger bond breakage. This reaction will need more energy so the activation energy will be increased. The same trend also found in final temperature variation, where the activation energy was increased as the final temperature increased as shown in Table 2. It was because the stronger bond of the molecule will be decomposed in high temperature.

c. Calorific value

Calorific value is the amount of energy released by a mass unit in combustion process(9). Calorific value of raw mahogany wood is 4410.77 cal/g while the calorific value of pyrolysis biochar were shown in Table 3.

TABLE 3. Calorific value of mahogany biochar yielded from pyrolysis

Bio-char						
Heating rate variation			Final temperature variation			
10°C/min	30°C/min	60°C/min	350°C	450°C	550°C	600°C
5633.51	6194.87	7512.96	6352.08	6194.87	6534.36	5910.05
cal/g	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g

Calorific value of bio-char was increased as the final temperature increased. As temperature increased, the composition of bio-char would close to pure carbon whose calorific value is about 32.8 MJ/kg (about 7872 cal/g) (10). In low temperature, the composition of solid product is not only char, but also the mixture of raw wood and char(2). Temperature was a factor that highly affect the calorific value of bio-char because in high temperature there would be more bound in cellulose and hemicellulose broken so the product would contain more pure carbon(11). The presence of ash can decrease the energy content so the calorific value would be decreased too(10). The lower calorific value at 600°C can be caused of this effect. At high temperature, the ash concentration will be increased and decrease the calorific value of biochar. Calorific value of biochar also raised at high heating rate. This was because at higher heating rate the sample would get more heat than at lower heating rate at the same minute. This heat would increase the decomposition reaction rate so there will be more carbon bound broken at the same time(12). All of the biochar yielded from pyrolysis have higher calorific value than its raw material. It shows that pyrolysis will increase the calorific value of a material. The calorific value of biochar also high enough so it can be developed as an environmentally friendly solid fuel.

CONCLUSION

Heating rate and final temperature were the factors that highly affect the activation energy and calorific value of a biochar. Activation energy decreased as the heating rate and final temperature increased. It shows that pyrolysis process will be easier to occur at high temperature. Calorific value of the biochar was higher than its raw material. The increasing of heating rate and final temperature will raised the calorific value of biochar. However the calorific value of biochar was decreased at 600°C because of ash formation. The highest calorific value of biochar was 7512.96 cal/g and was found at 450°C with heating rate of 60°C/min.

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